Site Need Statement General Reference Information Need Title: Sulfate Mitigation for Hanford Tank Low Activity Waste (LAW) Vitrification Need Code: RL-WT101 Need Summary: Sulfate, which is a significant component in the supernate fractions of many tank wastes at Hanford, poses serious economic impacts and risks for the LAW vitrification process. Sulfate tends to phase separate in the melter forming a corrosive molten sulfate salt layer on top of the glass melt that will damage the melter and negatively impact glass quality if allowed to accumulate. Improved glass and feed formulation for sulfate incorporation are required. Origination Date: FY 2001 (October 18, 2001) *Need Type*: Technology Need **Operation Office:** Office of River Protection Geographic Site Name: Hanford Site **Project:** Waste Treatment and Immobilization Plant PBS No: RL-TW06 National Priority: 1. <u>High</u> - Critical to the success of the EM program, and a solution is required to achieve the current planned cost and schedule. Medium - Provides substantial benefit to EM program projects (e.g., moderate to high life-cycle cost savings or risk reduction, increased likelihood of compliance, increased assurance to avoid schedule delays). 3. Low - Provides opportunities for significant, but lower cost savings or risk reduction, may reduce the uncertainty in EM program project success.

10 Operations Office Priority:

Problem Description Information

- Operations Office Program Description: Hanford tank wastes will be retrieved and delivered to the RPP-WTP where it will be separated during pretreatment into high level waste (HLW) and low activity waste (LAW) fractions, both of which will be immobilized by vitrification for disposal as glass in canisters.
- Need/Problem Description: Sulfate mitigation became a particularly important LAW vitrification issue for the RPP-WTP following a conclusion in January 2000 that it would not be practical to remove sulfate from LAW during pretreatment. An estimated 20% additional amount of ILAW glass is expected to be produced from sequentially processing all 177 tanks at the Hanford site. Blending of LAW feeds solutions could reduce the estimated increase in ILAW glass production.

Sulfate is only sparingly soluble in glass melts and tends to separate forming a corrosive molten sulfate salt layer on top of the glass melt in the melter that will damage the melter if allowed to accumulate. The primary sulfate mitigation approach will be to operate the RPP-WTP so as to prevent the formation of phase separated sulfate salts in the melter. Preliminary testing has indicated maintaining the glass $Na_2O * SO_3$ concentration product less than 5 wt% as a constraint for preventing sulfate salt separation. However, this empirical constraint can be affected by other composition variables and also depends on factors such as melt mixing and processing rate. For LAW derived from the higher sulfate content tanks, conservative processing constraints for sulfate will require substantial reductions in waste loading, increasing the quantity and cost of LAW glass to be produced and disposed of.

It is expected that sulfate, along with halide salts also contained in the LAW, will result in decreased melter life due to enhanced corrosion of critical materials, especially if a sulfate salt layer accumulates in the melter. Molten sulfate salts are electrically more conductive and lower viscosity than the glass melt creating a risk for electrical shorting. The composition of potential separated salt phases is also critical, in that low melting temperature salt mixtures may form allowing deep penetration of molten salts into the refractory package of the melter increasing the risk of electrical shorting. There is also concern that feeding slurry or water onto a molten sulfate layer in the melter could cause over pressurization or a steam explosion in the melter. However, the actual risks and impacts on melter life associated with sulfate in LAW are not well characterized.

Work done in prior waste vitrification programs to address sulfate issues have focused mainly on glass and

feed formulation to optimize sulfate incorporation by the glass. A broader approach to sulfate control and mitigation is embodied in the RPP-WTP Research and Technology Program. However, the resources currently available for this work are not adequate to cover the scope of needs. Further mitigation methods development is needed to allow process optimization and provide for risk reduction. Details for specific recommended development areas follow.

Glass and Feed Formulation: Glass formulations must meet both product specification and process ability requirements. Reduced waste loading glass formulations for sulfate that meet the "Waste Form Testing" specifications and the preliminary empirical glass $Na_2O * SO_3 < 5$ wt% constraint have been developed substituting other fluxing oxide glass former components for Na_2O . However, the composition and properties of sulfate phases that are formed when the sulfate incorporation thresholds (less than the glass solubility limits depending on melter dynamic factors) of these glasses are exceeded need to be considered. Mixed sulfate salts may be formed that are more corrosive than Na_2SO_4 and have lower melting temperatures, allowing deep penetration of the salts through joints and cracks in the melter refractory package creating electrical shorting and enhanced corrosion risks that may lead to melter failure. Sulfate salts potentially formed with candidate glass and feed formulations need to be characterized for composition, melting temperature range, electrical conductivity and corrositivity. Sulfate incorporation is also sensitive to feed conditioning additives used to control glass redox $(Fe^{+2}/Fe^{+3}$ ratio). Excessive feed reductant additions can lead to sulfide formation that can also damage the melter. There is a need to optimize the glass and feed formulation to allow for increased sulfur incorporation without unacceptable effects on process ability or product quality.

Materials and Melter Design: The baseline RPP-WTP LAW melter uses an active melt agitation system that aids sulfate incorporation into the glass. These agitation devices, and other refractory metal components such as thermowells, level detectors and airlift lances that enter the glass melt from above, have shown a tendency for corrosive failure primarily near the melt surface and require frequent replacement to prevent failure in the melter. The effects of sulfate salts on these components have not yet been well characterized. Possibly more important, the effects of sulfate phases that may be formed on non-replaceable melter materials such as refractories and critical metal components are not well understood. Some design modifications may also be needed for sulfate detection if a viable detection system is developed, or for a mechanical method for sulfate layer removal should process approaches for removal prove unsuccessful.

There is first a need to determine the tolerance of melter materials and components to sulfate salt exposure, which will likely depend on salt composition and properties yet to be determined. The best materials need to be identified and designs for critical components developed to increase their service life.

13 Functional Performance Requirements:

Glass and Feed Formulation

- Meet ILAW product specifications.
- Melt viscosity at 1150°C of 20-100 poise.
- Glass melt electrical conductivity compatible with power supply capabilities.
- Glass liquidus temperature <950°C.
- Not be corrosive to melter components.
- Will not form stable salt phases with melting temperatures below ~600°C.

Materials and melter design

- Consumable melter components should be designed to require minimal maintenance considering the potential for sulfate exposure and have a minimum replacement life before failure of two months.
- Refractory package design needs to consider properties (particularly melting temperatures, electrical conductivity and corrosivity) of salt layer phases potentially formed in the melter.
- Definition of Solution: The sulfate in LAW mitigation needs will be satisfied when: 1) reliable/cost effective detection methods have been developed that detect sulfate salt layers in the melter, 2) reliable/cost effective sulfate layer removal techniques have been developed, 3) glass/feed formulations have been optimized for waste loading, product properties and melter processability, and 4) materials and melter component designs have been developed that significantly improve the life of replaceable and non-

replaceable melter components in the presence of a sulfate layer. Targeted Focus Area: Tanks Focus Area **Potential Benefits:** The major benefit of these facilities is to ensure that the WTP starts up and operates according to plan and schedule: processing the various wastes in the quantities expected The primary benefit of solving these needs is cost savings. The presence of sulfate in the LAW feed to the melter is expected to increase the operating time and amount of LAW glass produced from minimum order quantity feeds by ~25%. Other benefits include reduced worker dose commensurate with the reduced operating time and reduced frequency of melter maintenance and replacement. Potential Cost Savings: **Potential Cost Savings Narrative:** Technical Basis: Current LAW glass formulations on the RPP-WTP Project are limited by the Na₂O * SO₃ concentration product less than 5 wt% constraint. This preliminary empirical constraint was developed by recent glass formulation and melter testing programs, and reduces potential waste loadings of some waste types (e.g., AZ-102 and AN-102) by more than 60%. An estimated 20% additional amount of ILAW glass is expected to be produced from sequentially processing all 177 tanks at the Hanford site. Blending of LAW feeds solutions could reduce the estimated increase in ILAW glass production. Cultural/Stakeholder Basis: The River Protection Project is committed to moving forward to design, construct, and put into operation the Waste Treatment and Immobilization Plant on the schedule recently agreed to in the Tri-Party Agreement. A robust program is necessary to ensure that delays, all of which are costly, are minimized. A key part of this risk mitigation is to include in the total program a capability to test with actual wastes the processes and equipment planned, or later in use. Environment, Safety, and Health Basis: A reduction in the amount ILAW product that needs to be processed, and less frequent melter maintenance and replacement campaigns, will result in less worker Regulatory Drivers: Environmental Impact Statement (EIS) for the Tank Waste Remediation System (TWRS) (DOE-RL and Ecology 1996) and the Hanford Federal Facility Agreement and Consent Order (known as the Tri-Party Agreement) and its amendments. DOE has negotiated additions to the Tri-Party Agreement that require the retrieval of single shell tanks by 2018, and the startup and operation of the WTP to support the treatment and immobilization of tank waste. By operating the WTP not only is that capability demonstrated and about 10% by volume (25% by activity) of the tank waste processed, but space is made available in the double shell tanks to allow the single shell tank retrieval to proceed without the expenditure of vast sums for additional double shell tanks. Other regulatory drivers include gathering the data necessary for the regulatory permits required for the startup and operation of the facility. November 15, 1999 tri-party agreement on principal regulatory commitments: • Start (Hot) commissioning-Phase I Treatment Complex 12/2007 • Start Operation-Phase 1 Treatment Complex 12/2009 • Complete Phase I-Treatment (no less than 10% of the tank waste by volume and 25% of the tank waste by activity) 12/2018 Other selected TPA milestones are: • Retrieve all SSTs 2018 Close SSTs 2024 Immobilize remaining tank waste 2028 • Close all tanks 2032 Material Streams: Hanford High-Level Defense Waste. The River Protection Project (formerly known as the Tank Waste Remediation System) involves PBSs RL TW-01 through TW-09. The technical, work scope definition, and intersite dependency risks for Phase 1 Waste Treatment and Immobilization is respectively, 3,3,3 on a scale of 1 to 5 where "5" represents high programmatic risk. This stream is on the critical closure path for Hanford Site cleanup. TSD System: Hanford Waste Treatment and Immobilization Plant. Technical risk is timely startup of this 25 plant and its ability to operate at planned throughput (capacity and operating efficiency). 26 Major Contaminants: Fission products, actinides, and nitrate. Contaminated Media: The LAW melters will be contaminated internally from the LAW glass and deposits from volatilized LAW constituents. The localized shielding enclosure of the LAW melters allows

- them to be contact maintained. The shielding enclosure will be sealed and externally decontaminated for spent melter disposal. Tank waste consisting of supernate (liquid), salt cake, and sludge.
- Volume/Size of Contaminated Media: The Hanford Site has 177 underground tanks that store 204 million liters (54 M gallons) of waste containing about 190 MCi of activity.
- 29 * Earliest Date Required: 9/2002
- 30 * Latest Date Required: 9/2005

Baseline Technology Information

Baseline Technology/Process: The current baseline technology for LAW sulfate mitigation is a conservative process approach that limits the waste loadings in LAW glasses such that the product of the wt% of Na₂O times the wt% SO₃ in the glass does not exceed 5. Glasses meeting this constraint are generally processable without formation of a sulfate salt layer. Baseline technologies have not yet been selected for melter sulfate salt layer detection or removal. The baseline LAW melter is the GTS Duratek locally shielded melter (LSM). No modifications have yet been made to the LSM design for LAW sulfate mitigation

Technology Insertion Point(s): N/A

- Life-Cycle Cost Using Baseline: The current baseline for the WTP is several billion dollars, with the BNI estimate itself is in the \$4 billion range. The current River Protection Project life cycle costs are estimated at approximately \$50 billion.
- Uncertainty on Baseline Life-Cycle Cost: There is large uncertainty in the WTP life-cycle cost, providing the opportunity to reduce the life-cycle cost due to operation improvements as well as ensuring operational success not to add additional cost to the system.
- 34 Completion Date Using Baseline:

Points of Contact (POC)

- 35 Contractor End User POCs:
 - Paul Rutland, River Protection Project Waste Treatment Plant, Process Technology Flowsheet, P/509-371-5213; F/509-371-5163; email: plrutlan@bechtel.com
 - Steve Barnes, River Protection Project Waste Treatment Plant, Research and Technology Vitrification Technology, P/509-371-5127, F/509-371-5163, email: smbarnes@bechtel.com
- 36 **DOE End User POCs:**
 - R. (Rudy) Carreon, DOE Office of River Protection Project Requirements Division, 509-373-7771, F/509-373-0628, email: Rodolfo Rudy Carreon@rl.gov
 - B.M. (Billie) Mauss, DOE Office of River Protection Program Office, 509-373-9876, F/509-372-2781, email: <u>Billie M Mauss@rl.gov</u>
 - E.J. (Joe) Cruz, DOE Office of River Protection Project Requirements Division, 509-372-2606, F/509-373-1313, email: E_J_Cruz@rl.gov
- 37 * Other Contacts:

^{*}Element of a Site Need Statement appearing in IPABS-IS